Davidson

Calorific Values Of American Woods.

CALORIFIC VALUES OF AMERICAN WOODS

BY

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THESIS

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THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1916

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 31st, 1916.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Carl Nathan Davidson

ENTITLED Calorific Values of American Woods

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Chemistry

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In Charge of Thesis

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Head of Department

Recommendation concurred in:*

	Committee on Final Examination*

*Required for doctor's degree but not for master's.

ACKNOWLEDGMENT

This investigation was carried on in the chemical laboratory of the University of Illinois during the collegiate years 1914- 1916. It was undertaken at the suggestion and has been carried out under the direction of Professor S. W. Parr.

The writer wishes to express his appreciation and most sincere thanks to Professor Parr for his patient kindness and valuable help so generously given.

He also wishes to thank Mr. J. M. Lindgren for his assistance and many helpful suggestions.

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Acknowledgment

CALORIFIC VALUES OF AMERICAN WOODS.

I.

It is the purpose of this investigation to review the calorific values assigned to woods of various types and to develop for AMERICAN woods a series of values which would be accurate within the limits of present day apparatus and manipulation.

It is true that wood as fuel is of minor importance but wood waste such as sawdust, slabs, etc. is not infrequently available, and the questiòn arises as to its relative heating value. Moreover, such data on American woods seems not to have been derived by investigators in this field. Indeed, it may be an open question as to whether any of the values accessible in the literature are of sufficiently recent or modern derivation to be accepted without question. A brief inspection of such values as are available and appear in fuel literature will at once raise the question of reliability, for example:

Among earliest investigations we naturally expect to find the work of Berthier. Some of the data worked out by Berthier is quoted in Groves and Thorpe, Chemical Technology Vol. I p. 360(1889) His work is confined to the use of the reducing power of organic matter on litharge, the theory being that the weight of lead reduced bore a constant relation to the amount of carbon present, whereby a constant could be deduced which multiplied by the weight of lead would give the amount of heat represented by the carbon present. The Berthier method is described in detail by Juptner(1)

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(1) Lehrbuch der Chem. Tech. der Energien - Juptner Vol.I part I- p. 115 (1905)

who indicates that it depends upon the quantity of oxygen necessary for the complete burning of the material and is based on the so-called Welter's law. Welter(2) believed that the union of one and the same quantity of oxygen with any of the elements gave the same amount of heat. Juptner(1) shows that this is not the case for when one kilogram of oxygen combines with carbon to form carbonic acid the amount of carbon consumed is 375 grams, having a heat value of 3030 calories. With hydrogen one kilogram of oxygen combines to form liquid water uniting with 125 grams with an accepted heat value of 4272 calories. Since Berthier assumes that the heat is generated by the union of carbon with oxygen, the values obtained by burning a carbon-hydrogen compound must be incorrect and the error must be greater the more hydrogen composing the material.

Another authority who has used this method and has published values for wood is Winkler. The Winkler values quoted in Groves and Thorpe(3) are calculated to the same basis of reference; namely, the number of pounds of water which would be raised from 0° to 100°C by one pound of wood. The Winkler values refer to wood said to contain 9 per cent of moisture but no evidence is given as to the method of determining the moisture present.

The Berthier and Winkler values referred to above are given in the following table.

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(2) The Calorific Power of Fuels - Poole p. 10 1898

(3) Chemical Technology Vol.I.p. 360. Groves and Thorpe.

TABLE I

Species	Berthier	Winkler
	Lbs. of H_2O heated from 0°-$100^{\circ}C$ by 1 lb. wood dried in ordinary manner.	Lbs. of H_2O heated from 0°-$100^{\circ}C$ by 1 lb. wood containing 9% H_2O.
1 part Oak	28.3	31.82
Beech	31.0	31.71
Ash	----	33.89
Birch	31.7	31.90
Pine	31.0	31.44
Fir	32.8	31.39

These valueshave little or no meaning in the present day literature which always refers to the heat developed by one pound of fuel as indicated by the rise in temperature of one pound of water; hence for purposes of comparison these data have been calculated over into modern terms as calories or the degrees centigrade which one pound of fuel would raise an equivalent weight of water. These table values may therefore be converted to calories by multiplying the number of pounds of water raised through 100°C by 100; this, in turn may be calculated into British Thermal units by multiplying by 1.8. Table II gives the converted values in terms of British Thermal units.

TABLE II.

	Berthier	Winkler
Species	B.T.U. lbs. Wood (said to be dried in ordinary manner)	B.T.U. lbs. Wood (said to have 9% moisture)
1 part Oak	5094	5728
Beech	5580	5708
Ash	----	6100
Pine	5580	5659
Fir	5904	5650
Birch	5706	5747

The next Experimenter was Count Rumford (4) (1813). In his work we have an indication that wood was subjected to actual combustion and the heat imparted to a measured quantity of water, thus comparing in principle to the present day methods. This work was carried out with shavings dried over a chafing dish. The calorimeter used was a crude affair; the piece of weighed wood being held by tongs under the open end of a tube and the products of combustion allowed to pass up the tube which was surrounded by water. When the rise in temperature, indicated by a thermometer, reached a certain point, the fire was put out and the amount of wood burned determined by subtracting the weight of the residue from the original weight.

Rumford's values, taken from Nicholson's Journal (4) are given in part in Table III. Here again the values need to be translated into the accepted standards of reference. Such calculations have

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(4) Nicholson's Journal 32: 105 (1813) 34: 319 (1813) 35: 95 (1813)

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been made and the corresponding values shown in Table III.

TABLE III.

Showing Values as Obtained by Rumford
with Calculations to B.T.U's per Pound.

1 lb. of Wood will heat	Pounds of H_2O from 0° - 100°C.	B.T.U. per pound of wood.
Lime tree (strongly dried over chafing dish)	40.131	7223.5
Beech "	36.746	6615.0
Elm "	34.083	6134.0
Oak "	29.880	5378.0
Ash "	35.449	6381.0
Fir "	37.379	6728.0
Poplar "	37.161	6689.0
Cherry "	36.904	6643.0

(5)

In 1836, Schödler and Petersen determined the heating values of various woods from the amount of oxygen necessary to burn one kilogram of wood. These results were also given in terms of pounds of water heated from 0° to 100°C by one pound of wood and they have also been translated to British Thermal Units as shown in Table IV.

They, however, carefully dried the wood to constant weight by mixing with copper oxide and drying in a current of air in a

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(5) Annalen der Chemie 17 : 139 (1836)

drying apparatus surrounded by boiling water. The wood was then burned and the carbon dioxide and water produced by the combustion were measured. From the quantities of carbon dioxide and water the amounts of carbon and hydrogen were calculated and the quantity of oxygen obtained by difference. The amount of oxygen required therefore, to burn one hundred pounds of the wood was then derived by subtracting the amount of oxygen contained in the wood from the total oxygen found in combination as CO_2 and H_2O. The heat values of the woods were said to be proportional to the oxygen required by the burning of the same. That is to say, if one hundred parts of hydrogen requires 800 parts of oxygen as indicated in their discussion, they concluded that the heat of combustion is greater because more oxygen was employed. But these values are not in the actual ratio of the heat developed by the burning of hydrogen and carbon, hence the theory reduces itself practically to that of Berthier. However, the data thus derived by these investigators has been calculated by Groves and Thorpe to the number of pounds of water raised from 0° to $100^{\circ}C$ by one pound of wood, and has already been given in Table IV.

Their method of calculations as we have seen is based on the same general principle as Bethier's except that a heat constant is taken and referred to a pound of oxygen instead of a pound of lead. Their theory must assume that a given amount of oxygen gives a definite amount of heat no matter what it combines with.

TABLE IV

Schödler and Petersen

	Lb. of H_2O heated from 0°-$100^{\circ}C$ by one lb. of wood.	(Said to be perfectly dried)	B.T.U. lb.wood (Calculated)
1 part Oak	39.82		7167.6
Beech	39.44		7099.0
Ash	39.76		7156.8
Birch	39.73		7347.6
Pine	40.82		7425.0
Fir	41.25		7151.4

The next experimenter seems to have been Emil Gottlieb (1885). He used wood which had been dried to constant weight at 115°C. His method was similar to our present day procedure using a calorimeter of the constant pressure type. That is, the wood was burned in a current of oxygen and the rise in temperature of the surrounding water noted. From this the heating value was calculated in British Thermal Units and knowing the percentage of moisture present he calculated his values to the dry basis. His results, therefore, are the most trustworthy to be found in the literature up to that date and they are the ones more frequently quoted in text books and books of reference. While subject to the limitations and possible errors due to incomplete combustion incident to burning in a current of oxygen they are the only values at all comparable with results available at the present time. His values, given in Table V which refer to fuel in the dry condition, are quoted from the J. Pratische Chemie, <u>28</u>: 412, (1883).

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TABLE V.

	B.T.U. per pound of dry wood
Oak	8316.
ASH	8480.
Elm	8510.
Beech	8591.
Birch	8586.
Fir(silver)	9063.
Pine	9153.

If now we compare the values obtained for woods for the same kind used by the different investigators we shall see wide discrepancies as shown in Table VI.

TABLE VI.

B.T.U. per pound of wood.

	Berthier (air dried) Berthier test	Winkler (calculated to dry basis) Berthier test	1813 Rumford (dried over chafing dish) (burned in air)	1836 Schodler (said to be "perfectly dry") Calculated from lbs. of O_2 to burn 1 kgm. wood	1883 Gottlieb (dry basis burned in stream of oxygen
Oak	5094	6294	7167.6	5378	8316
Beech	5580	6272	7099.0	6615	8591
Birch	5706	6309	7347.6	----	8586
Fir	5904	6208	7405.0	6728	9063
Pine	5580	6218	7347.6	----	9153
Ash	----	6703	7156.8	6381	8480

Referring to the results given in Table VI, the values of Berthier are shown to be only about half as great as those of

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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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Gottlieb. However, they are sufficiently near those of Winkler so that if it were possible to calculate them to the dry basis they might be at least measurably comparable with Winklers, whose results were derived by the same method. A comparison of Winkler's values with Gottlieb's shows that the results obtained by the former investigator would have to be increased about 50% in order to secure a value at all near those of Gottlieb. This in itself at once demonstrates the absurdity of Winklder's values and therefore also of Berthier's. This we might surmise from considerations already set forth in discussing the basis for the test which we have shown to be erroneous in principle.

Rumford's values are also from 40-50% at variance with Gottlieb's. He did not know the percent of moisture in his samples of wood and his calorimeter, if it can be called one, was a mere makeshift. Recalling his method it can readily be seen that his values can be given no standing whatever. Rumford's values, therefore, with those of Berthier and Winkler should be given no credence at all and should be repeated in the literature only to show the steps in the development of calorimetric methods.

If now we compare the results of Schödler and Petersen with those of Gottlieb we find large differences, which we would naturally expect from the above theoretical considerations. Schodler and Petersen's results have this virtue, however; that is, that they refer to wood which was carefully freed from water. The fact that they brought their values to the dry basis as shown in Table VI gives much better results than obtained by previous investigators but they are not near enough to the standard values of Gottlieb to be acceptable.

II.

Moisture Content and Its Determination.

The first thing which naturally presents itself after a study of the literature of calorific values is the importance of an accurate moisture determination. There is involved also the question as to whether or not wood can be thoroughly dried without decomposition; that is to say, can it lose all of the contained moisture and arrive at a constant weight. Different methods of drying give different results and we should know how much of the variations are due to the methods employed. It is possible that we may find as much uncertainty connected with the moisture determinations as we have found in connection with the estimation of heat values.

Juptner(7) says that two years of air drying reduces the moisture to 15-16%.

Soft woods(8) contain more water in the fresh state than hard woods but they lose it more easily and can be more thoroughly dried. The remaining moisture after air-drying, can only be expelled by heat and the last portions with such difficulty that the wood commences to decompose. The question then arises as to the maximum temperature to which wood may be heated before decomposition sets in.

Violette(7) showed that all the water was not removed by air-drying. He heated wood, which had been seasoned for two years, in a current of super-heated steam at 125°-225°C. Between 200° and 225° there was a slight carbonization and water alone was not given off. The results are shown in Table VII.

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(8) Grooves & Thorpe. Chem. Tech. -Fuels. p.4. (1889)

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TABLE VII.

Temp.	Oak	Ash	Elm	Walnut
125°	15.26	14.78	15.32	15.55
150°	17.93	16.19	17.02	17.43
175°	32.13	21.22	36.94	21.00
200°	35.80	27.51	33.38	41.77
225°	44.31	33.38	40.56	36.56

Judging from the much greater loss at 175° than at 150°C it appears as if the decomposition might have started between these temperatures.

Rumford(9) heated the following air-dried woods at a temperature of 136°C as long as they lost weight without being chemically changed, and found that 100 parts of the wood lost weight as shown in Table VIII.

TABLE VIII.

100 parts of

FIR	lost	17.53 parts
Oak	"	16.64 "
Elm	"	18.20 "
Beech	"	18.56 "
Birch	"	19.38 "

Rumford's data, if carefully and accurately obtained, would indicate that the temperature of decomposition is above 136°C.

F. P. Veitch(10) on the other hand says that, in the case of resinous woods, turpentine begins to distill at 97°C.

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(9) Grooves & Thorpe - Chem. Tech.- Fuels p.5 (1889)
(10)Circular 36. Bur. of Chem. U.S.Dept. of Agriculture.

Schodler and Petersen dried the powdered wood to constant weight at the temperature of boiling water and assumed the wood to be perfectly dry; Gottlieb did the same at 115°C.

It is evident from these data that the minimum point of decomposition has not been determined and that no standard method for the determination of moisture in wood is to be found. Such a method, however, is very essential for the determination of accurate calorimetric results. The first part of this investigation has been an effort to work out a satisfactory method for the determination of moisture in woods; a method which would completely free the material from water but would not cause decomposition. The point of maximum loss of moisture and minimum decomposition has been called the "dry point."

(a) Experimental:

The following methods for determining the moisture in wood were used because they have been found satisfactory in coal analysis.

A. Heating for sixty minutes in a constant temperature oven at 104°-110°C in a current of dry air or preferably an inert atmosphere such as carbon dioxide or nitrogen.(11)

B. Heating for 30 minutes at 135° - 140° C*.

A comparison of the results obtained by methods A and B with coal is given in Table IX.

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(11) Proc. Am. Soc. Test. Mat. Report of Sub. Comm. II on Moisture Determination in Coal. 14: part 2, 419 (1912)

(*) J. Franklin Instit. Feb. 1912. John White.

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TABLE IX.

Comparison of Moisture Determinations.

Lab. No.	Kind	Method B White Xylene Oven for 30 min. at 137°C	Method A (Am. Soc. Test. Mat. Meth) Freas Oven 1 hr. at 105°C
6382	Lignite	8.46 %	8.78
6453	Anthracite	1.57	1.27
6517	Bituminous	2.78	2.92
6518	"	2.80	3.02
6519	"	4.00	4.08

Weighed samples (about 1 gram) of kiln dried yellow pine, oak, birch, poplar, cherry and hickory in the form of sawdust were heated at 105° C and 137°C each for 1,2,3,4,5,6 and 7-hour periods using a new sample for each period. All samples were cooled twenty minutes over concentrated sulfuric acid before weighing. The loss in weight determined by difference was taken as moisture.

A. A Freas electric oven was used the inside compartment of which measured 12" x 12" x 12". In one set of determinations oxygen free carbon dioxide* dried by washing with concentrated sulfuric acid, was passed through at such a rate that the atmosphere was changed about ten times per hour, thus keeping about ninety per cent carbon dioxide present during the run. In another series, air-dried in the same way, was passed through at the same rate. In all cases the samples were contained in glass capsules (11) (2 cm x 2 cm) which were covered with ground glass caps as soon as taken from the oven.

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* Analysis of the Compressed Co_2 gave 1.32% O_2.

The results of the moisture determinations are graphically shown in charts, a to h in which the loss in weight, as ordinate, is plotted against the time in hours; the temperature and atmosphere being the variables.

Discussion of Curves.

A study of the results as given in detail by the curves seems to establish certain facts as follows:

1.- The total loss in weight of allthe woods is arrived at and a substantially constant weight secured at 105°C in either air or carbon dioxide and practically no variation occurs on prolonged drying through seven hours, the limit of the test.

2.- Since the loss in weight in air is substantially the same as in carbon dioxide for the prolonged periods of heating, it is assumed that there is no oxidation at that temperature.

3.- The curves in Figure III show that the total loss and a constant weight are obtained at 137°C in air or carbon dioxide and that practically no variations occur on heating through the seventh hour.

4.- There is no oxidation at 137°C in an atmosphere of air. This statement is based upon the fact that the changes in loss of weight are substantially the same in both carbon dioxide and air.

5.- There is a small difference between the loss in volatile constituents at 137°C and the loss at 105°C. The statement is based on the fact that the loss in both air and carbon dioxide at 137°C is slightly greater than the loss in air and carbon dioxide at 105°C. Whether the additional loss at 137°C is moisture or volatile organic constituents is an open question, at any rate, it does not amount

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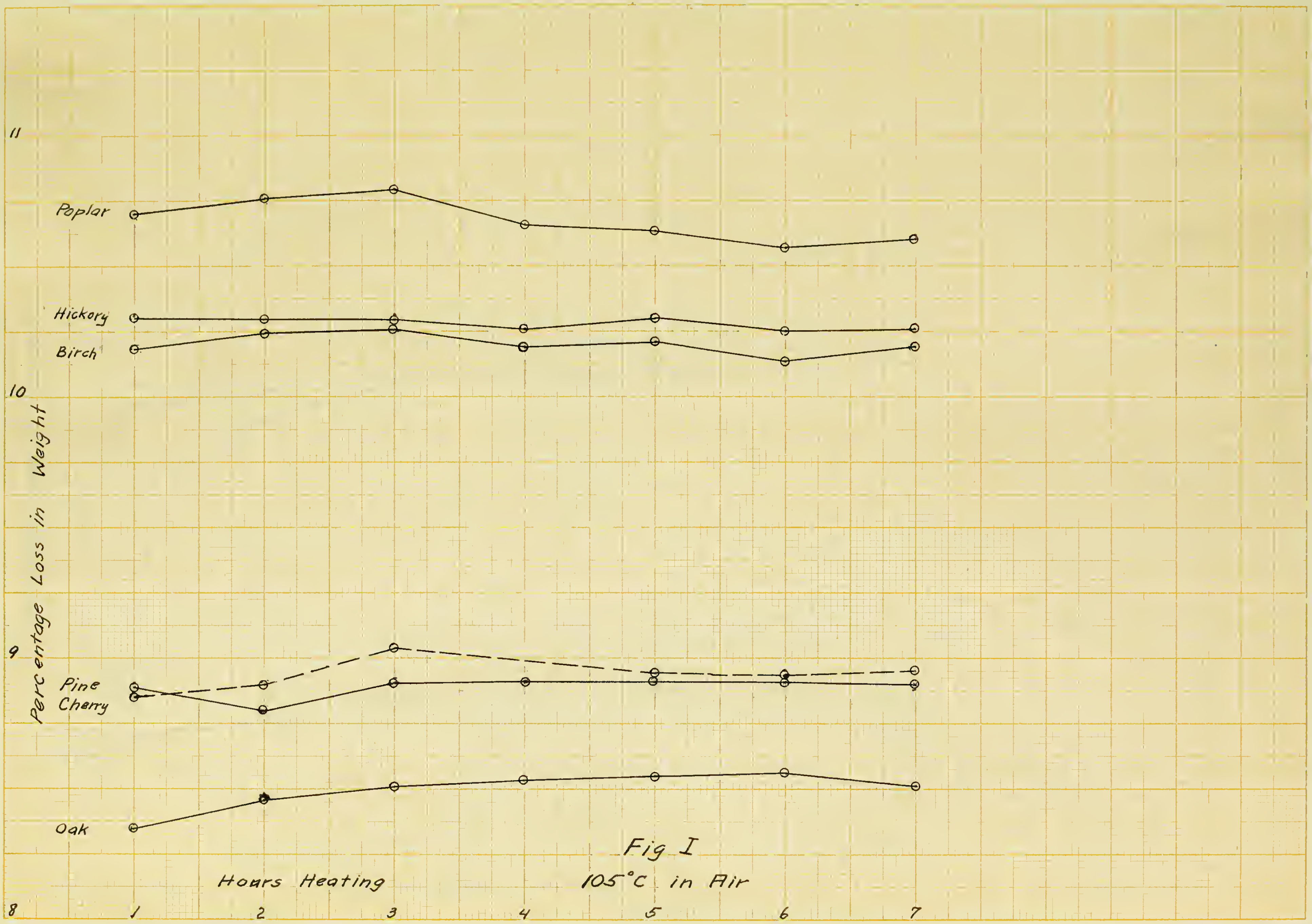

Fig I
105°C in Air

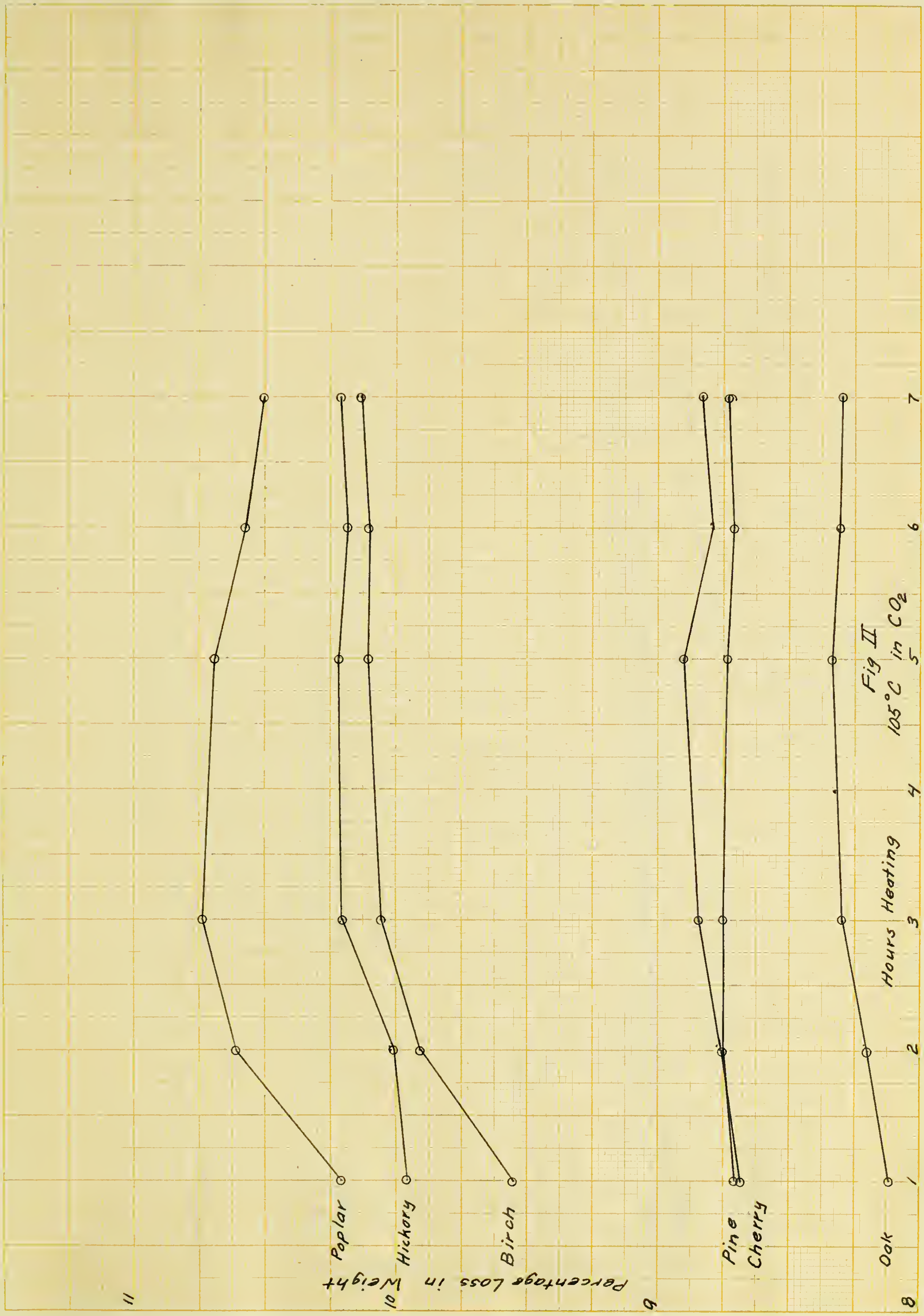

Fig II
105°C in CO2

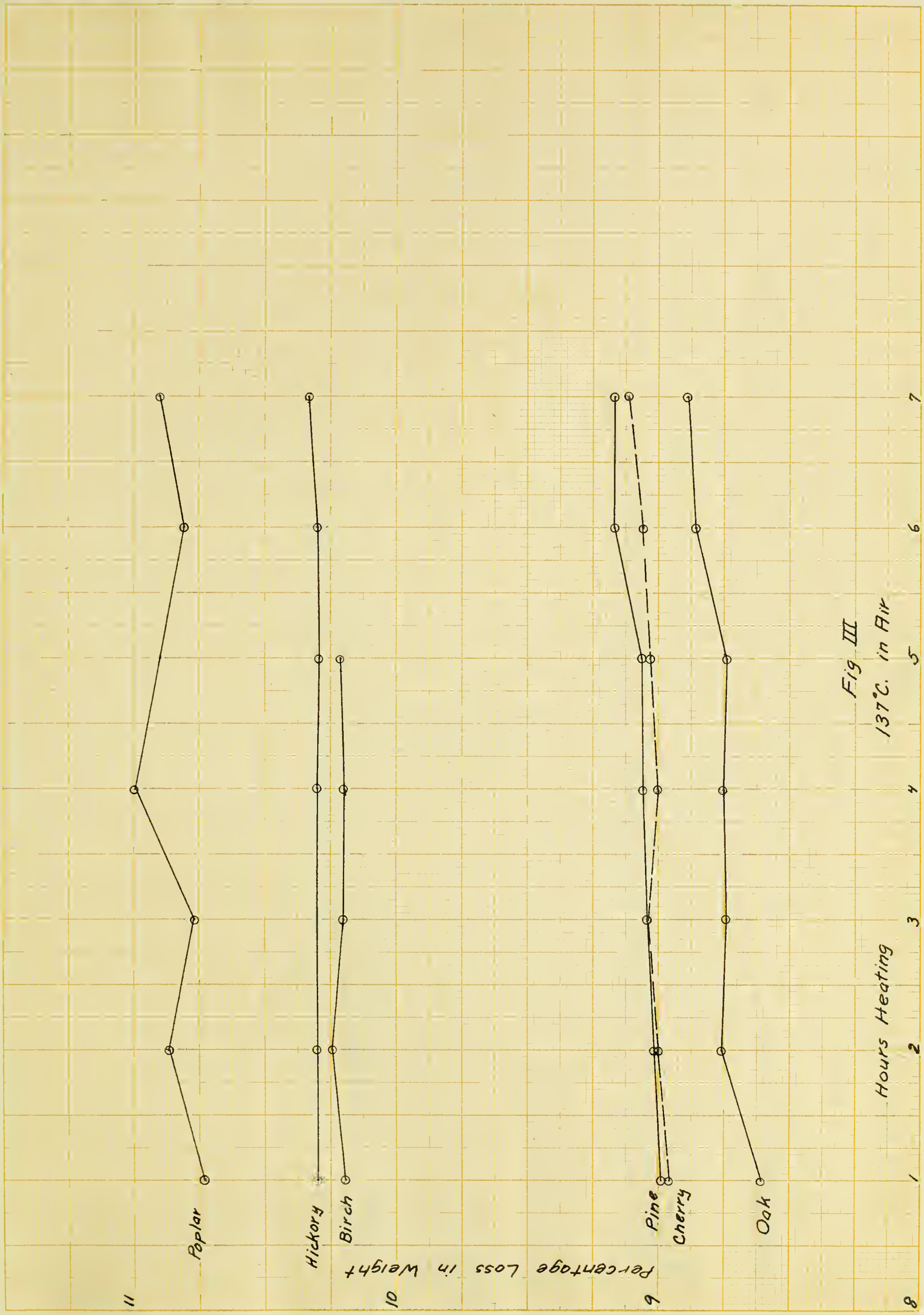

Fig III
137°C. in Air

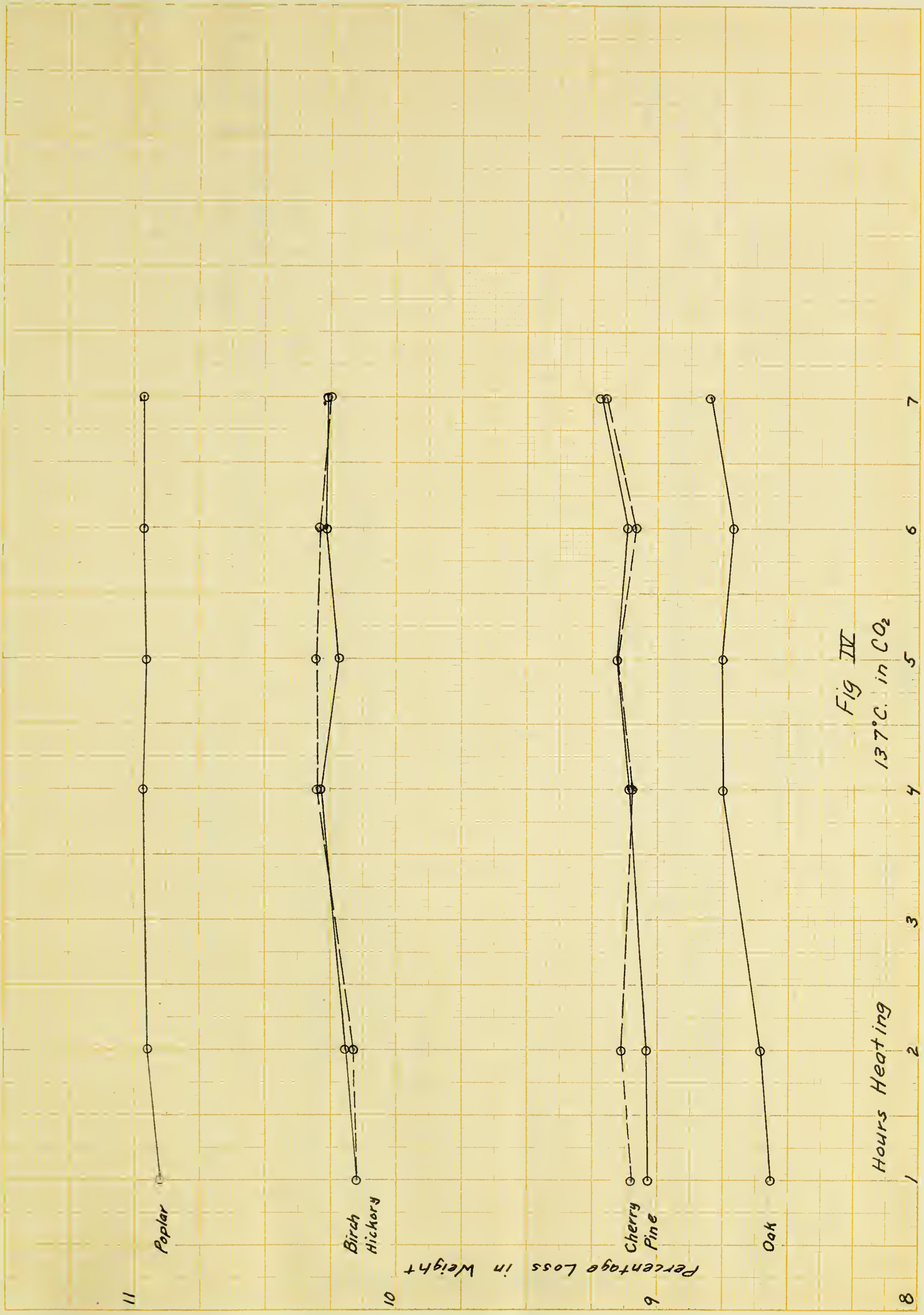

Fig IV
137°C. in CO₂

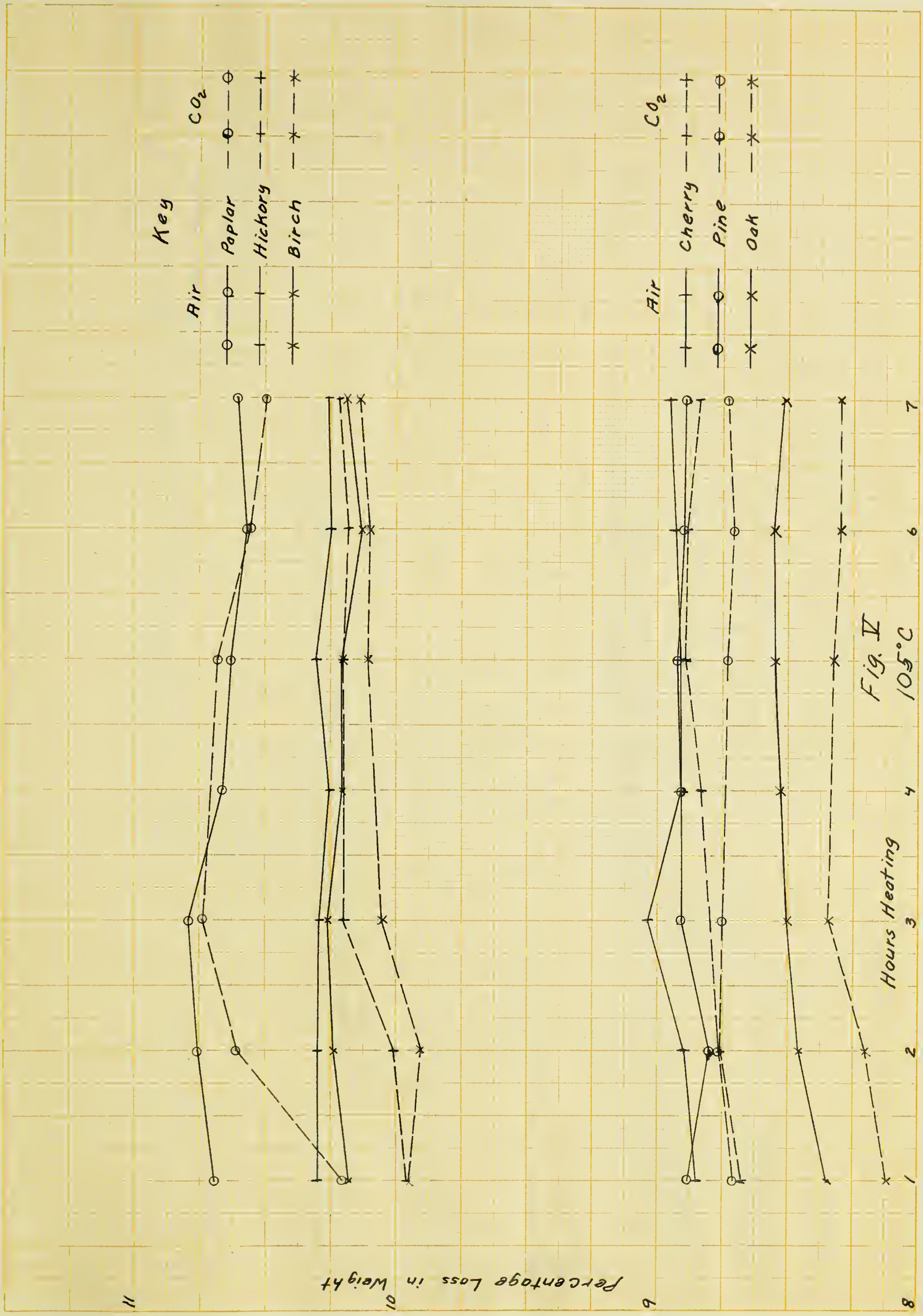

Fig. V
105°C

Key
Air
CO2
Poplar
Hickory
Birch
Air
CO2
Cherry
Pine
Oak
Percentage Loss in Weight
11
10
9
8
Hours Heating
1
2
3
4
5
6
7

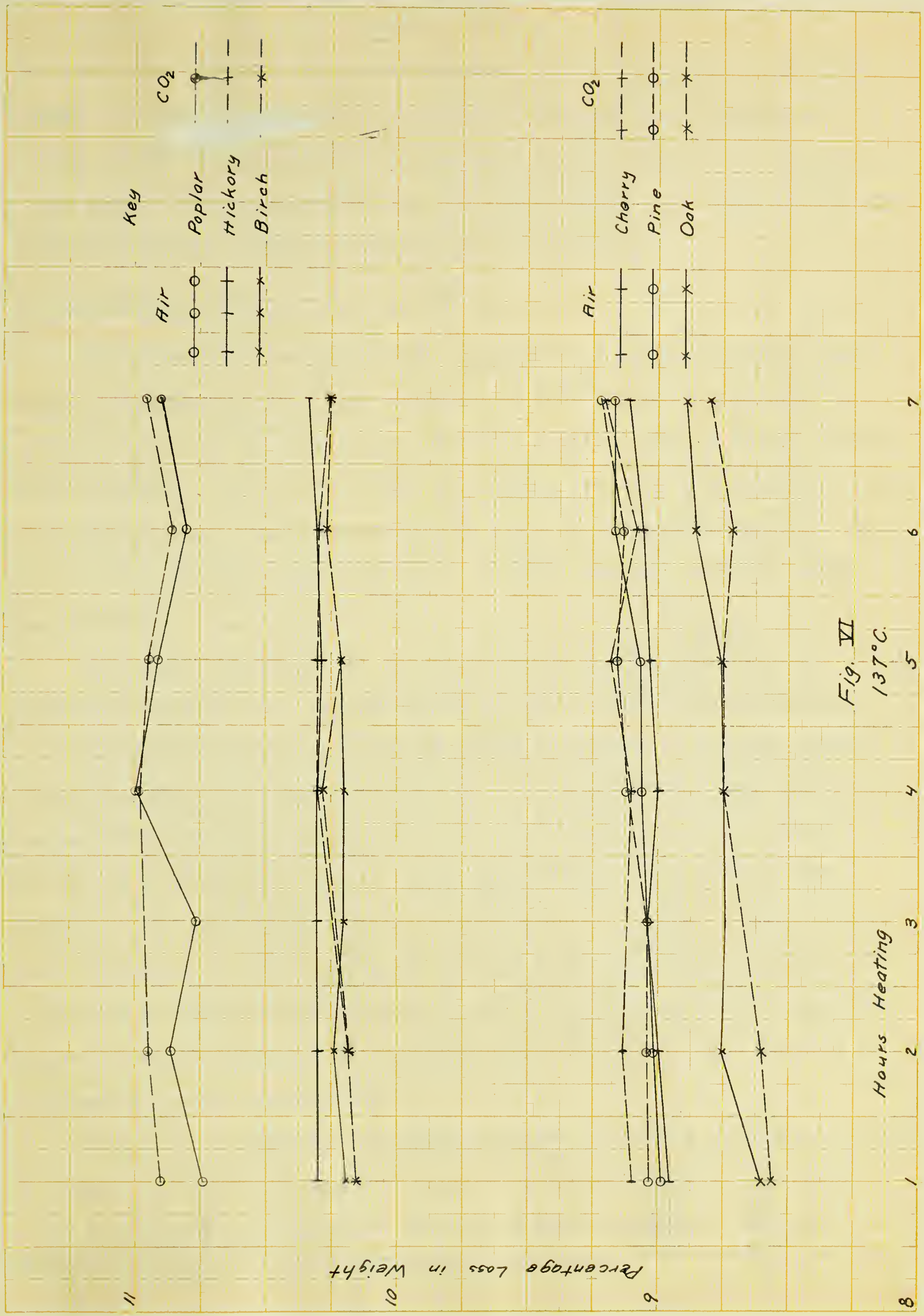
Key
Air
CO$_2$
Poplar
Hickory
Birch
Cherry
Pine
Oak
Percentage Loss in Weight
11
10
9
8
Hours Heating
1
2
3
4
5
6
7

Fig. VI
137°C.

to more than .3 percent on the average for seven hours of heating. Since all the water should be given off at 105°C and indeed we would expect to find volatile organic constituents at the temperature used, it is altogether probable that this extra loss represents certain volatile organic substances in the wood.

B. Products of Distillation at 137°C.

This test was used with the intention of collecting the products constituting the loss in weight at 137°C and if possible to obtain some idea of the nature of the products which are not driven off at 105°C. This part of the study was not very satisfactory in that the nature of the constituents was not exactly determined. It was found, however, that the loss at 137°C was not entirely made up of water.

The apparatus used was a modified form of White's(12) drying apparatus (Plate I.) A temperature of 135°- 140°C was maintained in a horizontal glass tube (A) by passing vapors of boiling xylene through a jacket (B) surrounding it. The condensed vapors were returned through a side arm (C) to the flask (D) which was heated by an electric oven (E). The temperature was kept constant by controlling the current by means of a rheostat. Connections a,b,and c were effected by means of mercury seals which prevented leakage of the vapors. These modifications of Prof. White's original apparatus, secured better circulation of vapors and prevented loss of material through the cork connections.

In order to measure quantitatively the products driven off from the wood, a stream of dry air free from carbon dioxide was passed over the boat containing the sample and then through a train of

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(12) J. Franklin Instit. Feb. 1912. John White

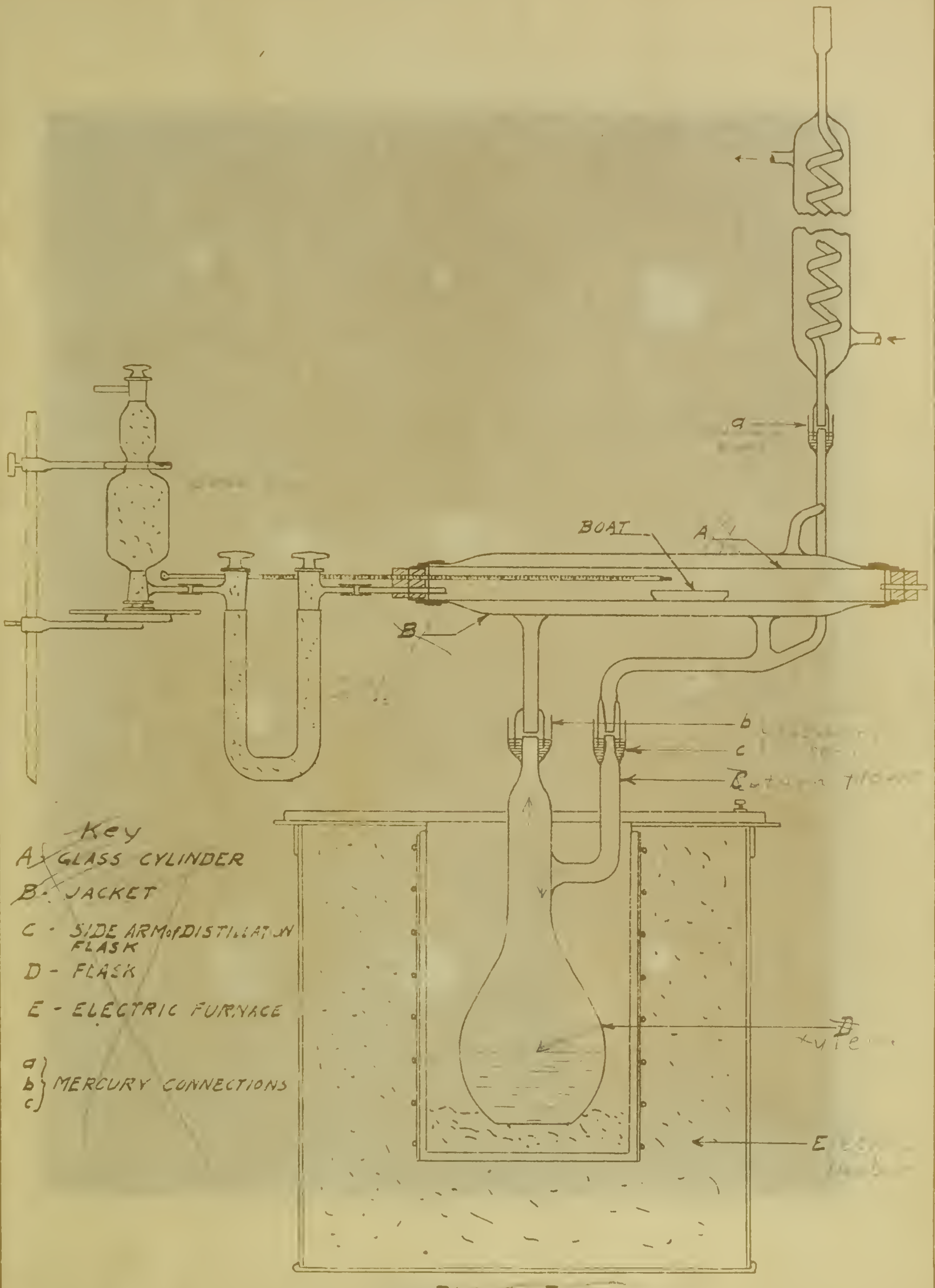
BOAT
A
B
a
b
c
C
D
E
Key
A - GLASS CYLINDER
B - JACKET
C - SIDE ARM of DISTILLATION FLASK
D - FLASK
E - ELECTRIC FURNACE
a
b } MERCURY CONNECTIONS
c

PLATE I

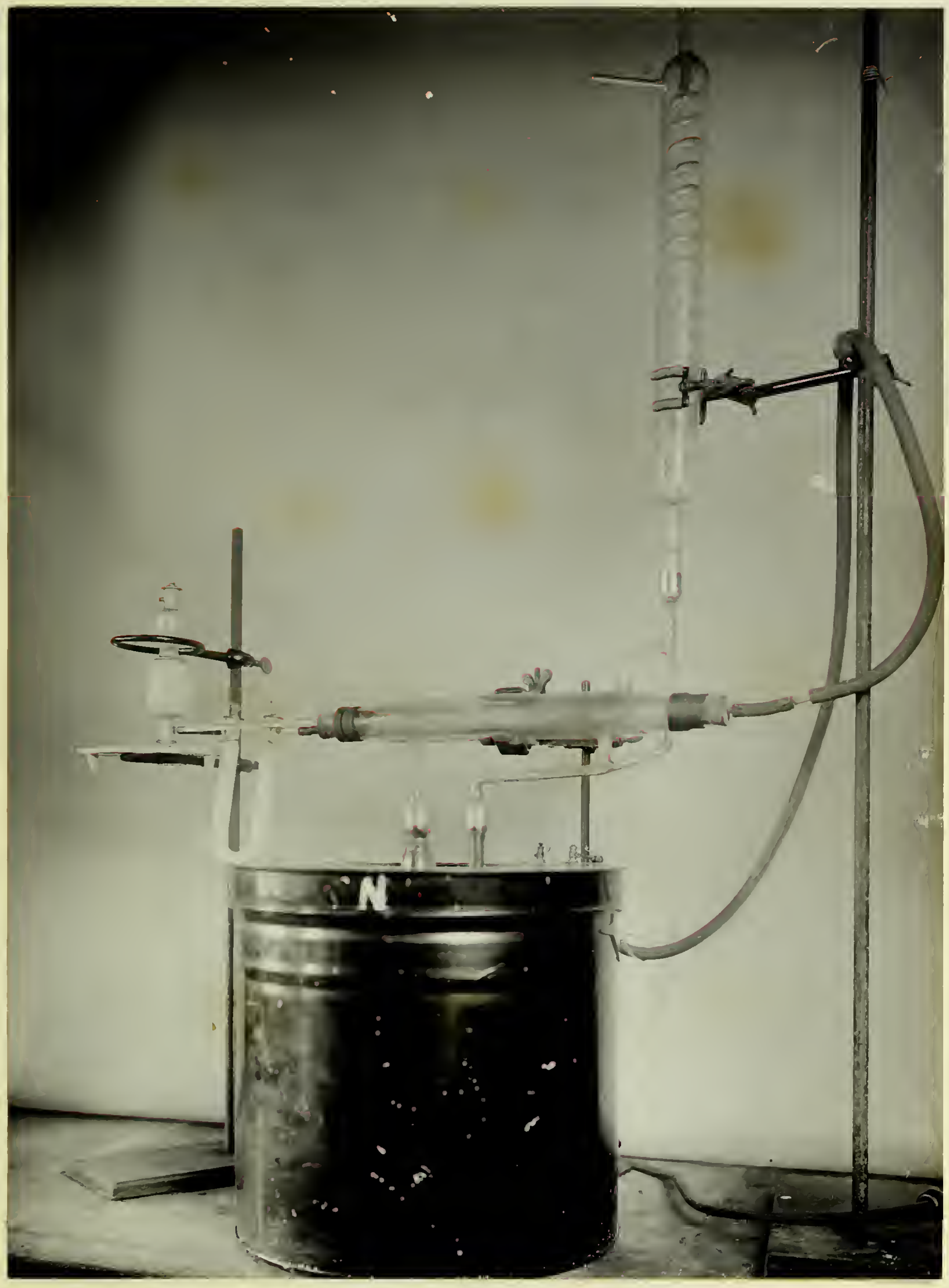

Plate I.

absorption bulbs.

Several types of bulbs and absorption agents were used but the best results were obtained by the use of sodalime contained in a Fleming bulb for carbon dioxide, and a mixture of coarse and finely powdered fused $CaCl_2$ in a U tube for the moisture.

When Liebig or Vanier bulbs containing potassium hydroxide were used the blank determinations were very unsatisfactory.

The data obtained are shown in Tables X and XI.

TABLE X.

Time of heating, One hour.

Wood	Percent of loss in weight. (By difference in weight of boat)	Percent H_2O absorbed. in P_2O_5	Change in weight of Fleming bulb.
Pine	9.04	7.45	Gain .0033 grams
	9.08	8.68	Loss .0009 "
	8.96	2.78	Gain .0044 "
	9.06	----	----
	9.10	8.23	Loss .0040 "
	8.99	8.57	" .0168 "
	9.05	----	" .0054 "
	9.00	8.89	" .0619 "
Oak	8.67	8.00	Loss .0002 "
	8.75	----	Gain .0013 "
	8.50	7.63	" .0115 "
	8.95	8.20	" .0050 "
	8.73	7.52	" .0004 "
	8.70	7.96	" .0011 "
	8.72	8.08	" .0001 "


THE
PARR OXYGEN BOMB
CALORIMETER
MFD. BY
THE STANDARD CALORIMETER Co
EAST MOLINE, ILL., U.S.A.
PATENTS APPLIED FOR
NO.

Plate II.

TABLE XI.

$CaCl_2$ tube blank = +.0006 grams

Fleming blank = +.0007 grams.

WOOD	Percent of loss in weight	Percent H_2O absorbed by $CaCl_2$ Corrected for blank	Change in wt. of Fleming bulb. Corrected for blank.	Percent CO_2
Oak	8.64	7.44	loss .0044	negative
	8.30		gain .0012	0.13
	8.40	7.85	" .0006	0.07
	8.62	----	none	negative
	8.72	8.30	gain .0006	0.08
	8.65	8.32	none	negative

III.

Calorific Values and Summary.

In this study the calorific values are given on the dry basis. They were determined on the samples of wood "as received" and then corrections were made for the percent of moisture. This may be determined by heating in air at 105° for one hour as shown in the foregoing discussion of the moisture curves. The results calculated to the dry basis are given in Table XII.

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	----	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	

[illegible]

[illegible]

[illegible]

TABLE XII.

Wood	Percent H_2O (105°Air for1 Hour	B.T.U.(as received)	B.T.U. (Dry Basis)
Pine	8.88%	8,040. 8,055.5 8,054.	
		Av. 8,049.8	8836.2
Oak	8.35%	7,829. 7,855.5 7,840.	
		Av. 7,841.5	8555.7
Hickory	10.30%	7,594.2 7,561. 7,578.8	
		Av. 7,578.	8448.1
Cherry	8.85%	7,852. 7,867.7 7,860.	
		Av. 7,859.9	8623.0
Birch	10.18%	7,607.2 7,593.0 7,592.2	
		Av. 7,597.4	8458.4
Poplar	10.69%	7,709.8 7,726.2 7,712.5	
		Av. 7,716.1	8639.6

The instrument used was of the adiabatic type of the Parr Oxygen Bomb calorimeter. Plates II and III. Corrections have been made for the heat of combustion of the fuse wire and for

Plate III.

the heat of formation of the nitric acid produced in the reaction according to the standard method for coal analysis given in the Proceedings of the American Society of Testing Materials (1914) Part 2- Coal Analysis.

Table XIII gives a comparison of those woods of the same variety as those used by Gottlieb, only three varieties are thus duplicated.

TABLE XIII.

	Gottlieb B.T.U.		Difference
Oak	8316	8555.7	+ 239.7
Pine	9153	8836.0	- 317.0
Birch	8586	8458.4	- 127.6

An inspection of the table shows that the results agree to within 1-1/2 to 3 percent referred to the results obtained in this work as standard. The fact that some of these results are plus and some minus and the woods used by the two lines of investigation were obtained in different countries, is evidence that the two sets of values are in substantial agreement. However, it must be concluded, considering the amount of work involved in the determination of moisture and the excellent checks obtained by an adiabatic calorimeter which has not heretofore been made use of in this work, it would seem that the statement is fairly well established to the effect that these values represent the correct heat values for the several samples worked on, and may be taken as fairly representative for American woods.

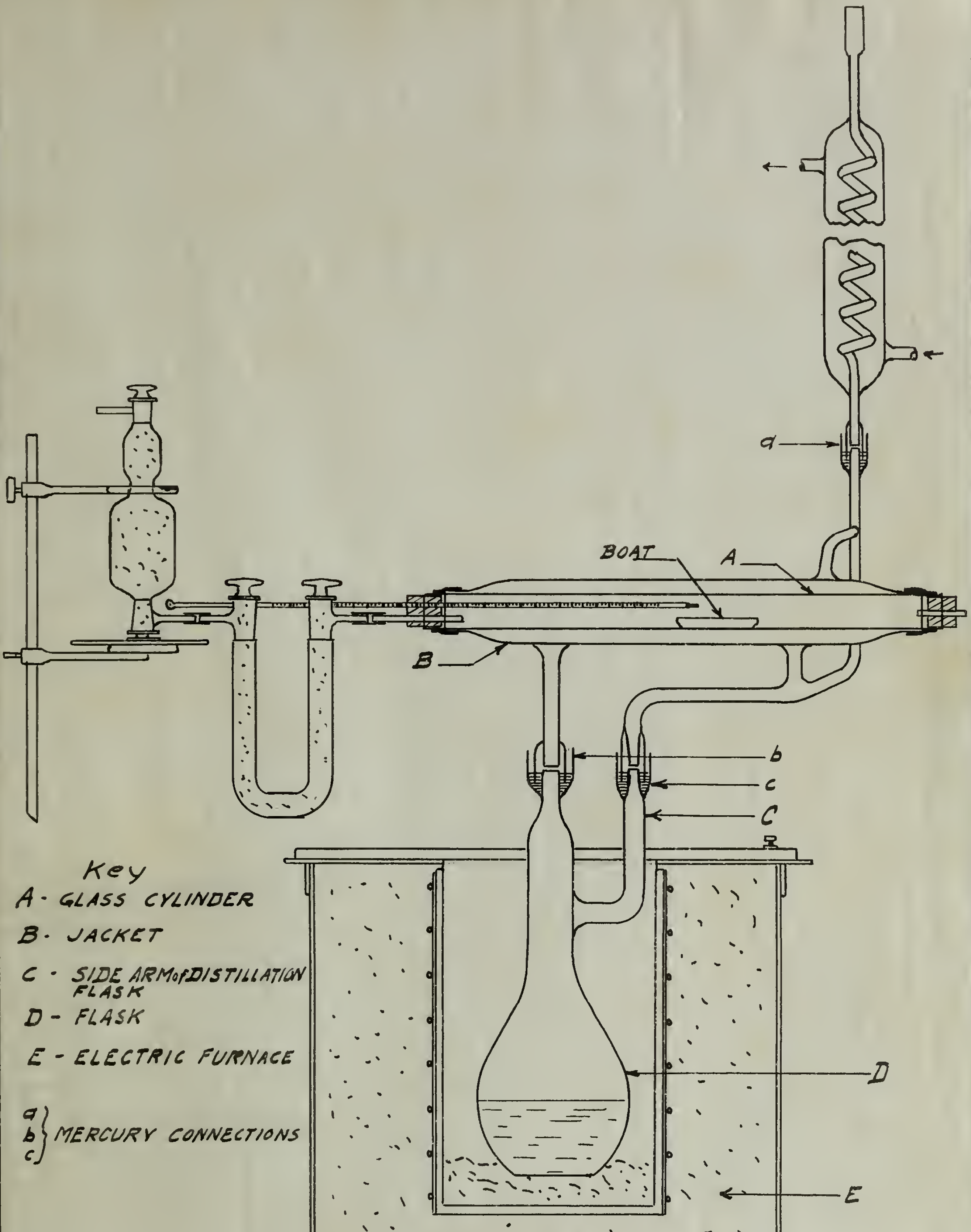
BOAT
A
B
a
b
c
C
D
E
Key
A - GLASS CYLINDER
B - JACKET
C - SIDE ARM of DISTILLATION FLASK
D - FLASK
E - ELECTRIC FURNACE
a
b
c
MERCURY CONNECTIONS

PLATE I